

We claim:

5 1. A process for preparing optionally alkyl-substituted 1,4-butanediol by two-stage catalytic hydrogenation in the gas phase of C₄-dicarboxylic acids and/or of derivatives thereof having the following steps:

10 a) introducing a gas stream of a C₄-dicarboxylic acid or of a derivative thereof at from 200 to 300°C and from 10 to 100 bar into a first reactor or into a first reaction zone of a reactor and catalytically hydrogenating it in the gas phase to a product which contains mainly optionally alkyl-substituted γ -butyrolactone;

15 b) introducing the product stream obtained in this way into a second reactor or into a second reaction zone of a reactor at a temperature of from 140°C to 260°C and catalytically hydrogenating it in the gas phase to optionally alkyl-substituted 1,4-butanediol;

20 steps a) and b) being carried out at the same pressure;

c) removing the desired product from intermediates, by-products and any unconverted reactant;

25 d) optionally recycling unconverted intermediates into one or both hydrogenation stages,

30 said hydrogenation stages each using a catalyst which comprises $\leq 95\%$ by weight, preferably from 5 to 95% by weight, in particular from 10 to 80% by weight, of CuO, and $\geq 5\%$ by weight, preferably from 5 to 95% by weight, in particular from 20 to 90% by weight, of an oxidic support, and

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the product mixture removed from the first hydrogenation stage being introduced without further purification into the second hydrogenation stage.

2. A process as claimed in claim 1, wherein the entrance temperature into the second reactor or into the second reaction zone of a reactor is lower than the entrance temperature into the first reactor or into the first reaction zone.
3. A process as claimed in claim 1 or 2, wherein the entrance temperature into the first reactor is from 235 to 270°C and the entrance temperature into the second reactor is from 160°C to 225°C, in particular from 180 to 200°C.
4. A process as claimed in any of claims 1 to 3, wherein the hot spot temperature in the first reactor is from 210 to 310°C, preferably from 245 to 280°C, and the process is carried out in such a manner that the hot spot temperature is above the entrance temperature and the exit temperature of the reaction gases, and is from 5 to 30°C, in particular from 5 to 15°C, more preferably from 5 to 10°C, above the entrance temperature.
5. A process as claimed in any of claims 1 to 4, wherein the pressure in both the first hydrogenation stage and the second hydrogenation stage is from 10 to 100 bar, preferably from 15 to 50 bar.
6. A process as claimed in any of claims 1 to 5, wherein the catalyst hourly space velocity of the first hydrogenation stage is in the range from 0.02 to 1, in particular from 0.05 to 0.5, kg of reactant/l catalyst • hour, and the catalyst hourly space velocity of the second hydrogenation stage is in the range from 0.02 to 1.5, in particular from 0.1 to 1, kg of reactant/l of catalyst • hour.
7. A process as claimed in any of claims 1 to 6, wherein the hydrogen/reactant molar ratio in both reaction stages is ≥ 5 , preferably from 20 to 600.

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8. A process as claimed in claim 7, wherein the hydrogen/reactant ratio in the first stage hydrogenation is from 20 to 200, preferably from 40 to 150, in particular from 50 to 100.
- 5 9. A process as claimed in any of claims 1 to 8, wherein the reactors used are selected from the group consisting of tubular reactors, shaft reactors, reactors having internal heat removal means, preferably tube bundle reactors and fluidized bed reactors.
- 10 10. A process as claimed in claim 9, wherein a tube bundle reactor is used in the first hydrogenation stage.
11. A process as claimed in claim 9 or 10, wherein a shaft reactor is used in the second hydrogenation stage.
- 15 12. A process as claimed in any of claims 1 to 11, wherein more than one reactor connected in parallel or in series is used in the first and/or second hydrogenation stage.
- 20 13. A process as claimed in any of claims 1 to 12, wherein a two-zone reactor is used.
14. A process as claimed in any of claims 1 to 13, wherein the process is carried out in an apparatus having a hydrogenation cycle and a compressor.
- 25 15. A process as claimed in any of claims 1 to 14, wherein the support material of the catalyst is selected from the group of ZnO, Al₂O₃, SiO₂, TiO₂, ZrO₂, CeO₂, MgO, CaO, SrO, BaO and Mn₂O₃ and mixtures thereof, preferably from the group of ZnO/Al₂O₃ mixtures, the delta-, theta-, alpha- and eta-modifications of Al₂O₃ and also mixtures which comprise at least one component each firstly from the group of
- 30 SiO₂, TiO₂, ZrO₂, and secondly from the group of ZnO, MgO, CaO, SrO and BaO.

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16. A process as claimed in any of claims 1 to 15, wherein the support material is selected from ZnO, ZnO/Al₂O₃ mixtures in a weight ratio of from 100:1 to 1:2 and mixtures of SiO₂ with MgO, CaO and/or ZnO in a weight ratio of 200:1 to 1:1.
- 5 17. A process as claimed in any of claims 1 to 16, wherein the catalyst comprises one or more further metals, preferably Pd, or a compound of one or more further metals, preferably an oxide, from groups 1 to 14 of the Periodic Table.
- 10 18. A process as claimed in any of claims 1 to 14, wherein the catalyst is used in the form of shaped bodies, preferably in the form of extrudates, ribbed extrudates, tablets, rings, spheres or spall.
- 15 19. A process as claimed in any of claims 1 to 18, wherein the BET surface area of the copper catalysts in the oxidic state is from 10 to 300 m²/g, preferably from 15 to 175 m²/g, in particular from 20 to 150 m²/g.
- 20 20. A process as claimed in any of claims 1 to 19, wherein the copper surface area of the reduced catalyst in the installed state is > 0.2 m²/g, preferably > 1 m²/g, in particular > 2 m²/g.
21. A process as claimed in any of claims 1 to 20, wherein the catalysts used in the first and second reactors are identical or different, preferably different.
- 25 22. A process as claimed in any of claims 1 to 21, wherein the shaped bodies of the catalyst used have a pore volume of ≥ 0.01 ml/g for pore diameters of > 50 nm, preferably of ≥ 0.025 ml/g for pore diameters of > 100 nm and in particular of ≥ 0.05 ml/g for pore diameters of > 200 nm.
- 30 23. A process as claimed in any of claims 1 to 12, wherein the shaped bodies of the catalyst used have a ratio of micropores having a diameter of > 50 nm to the total pore volume for pores having a diameter of > 4 nm of > 10%, preferably > 20%, in particular > 30%.

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24. A process as claimed in any of claims 1 to 23, wherein the reactant used in the reaction is maleic anhydride.
25. A process as claimed in any of claims 1 to 24, wherein maleic anhydride is used which has been prepared by oxidizing benzene, C₄-olefins or n-butane, and the crude maleic anhydride obtained by oxidation has been extracted from the crude product mixture using a solvent (absorbent) and then stripped from this solvent using hydrogen.
26. A process as claimed in any of claims 1 to 25, wherein the absorbent is selected from the group consisting of tricresyl phosphate, dibutyl maleate, high molecular weight waxes, aromatic hydrocarbons having a molecular weight of from 150 to 400 and a boiling point above 140°C, preferably dibenzene, di-C₁-C₄-alkyl esters of aromatic and aliphatic dicarboxylic acids, preferably dimethyl 2,3-naphthalenedicarboxylate and/or dimethyl 1,4-cyclohexanedicarboxylate, methyl esters of long-chain fatty acids having from 14 to 30 carbon atoms, high-boiling ethers, preferably dimethyl ethers of polyethylene glycol, preferably of tetraethylene glycol, and alkyl phthalates and dialkyl phthalates having C₁-C₁₈-alkyl groups, preferably from the group of dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di-n-propyl and diisopropyl phthalate, undecyl phthalate, diundecyl phthalate, methyl phthalate, ethyl phthalate, butyl phthalate, n-propyl and isopropyl phthalate.
27. A process as claimed in any of claims 1 to 26, wherein the maleic anhydride is stripped from the absorbent under reduced pressure or pressures which correspond to the hydrogenation pressure or are a maximum of 10% above this pressure.
28. A process as claimed in any of claims 1 to 27, which is carried out batchwise, semicontinuously or continuously, preferably continuously.